Remote Sensing of Environment 200 (2017) 89–101

Contents lists available at ScienceDirect

Remote Sensing of Environment

journal homepage: www.elsevier.com/locate/rse

Pan-Arctic optical characteristics of colored dissolved organic matter: Tracing dissolved organic carbon in changing Arctic waters using satellite ocean color data

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ARTICLE INFO

Keywords:
CDOM
DOC
Ocean color
Arctic Ocean

ABSTRACT

Light absorption of the colored fraction of dissolved organic matter (CDOM) is a dominant optical component of the Arctic Ocean (AO). Here we show Pan-Arctic characteristics of CDOM light absorption for various Arctic regions covering both coastal and oceanic waters during the Tara Oceans Polar Circle expedition. The Siberian (or eastern) side of the AO is characterized by higher CDOM absorption values compared to the North American (or western) side. This is due to the difference in watersheds between the eastern and western sides of the AO and is consistent with an Arctic absorption database recently built by Matsuoka et al. (2014). A direct comparison between *in situ* and satellite data demonstrates that CDOM absorption is derived Arctic-wide from satellite ocean color data with an average uncertainty of 12% (root mean square error of 0.3 m^{-1}) using our previously published algorithm. For river-influenced coastal waters, we found a single and highly significant relationship between concentrations of dissolved organic carbon (DOC) and CDOM absorption ($r^2 > 0.94$) covering major Arctic river mouths. By applying this *in situ* relationship to satellite-derived CDOM absorption, DOC concentrations in the surface waters are estimated for river-influenced coastal waters with an average uncertainty of 28%. Implications for the monitoring of DOC concentrations in Arctic coastal waters are discussed.

1. Introduction

Colored dissolved organic matter (CDOM) refers to the fraction of the dissolved organic matter pool that absorbs light in water, and is quantified by its spectral absorption coefficient [m^{-1}]. CDOM plays a variety of roles in ocean physical and biogeochemical processes (e.g., Moran and Zepp, 1997; Miller et al., 2002; Matsuoka et al., 2012, 2015) and provides the possibility to trace, using a simple optical measurement, the concentration of dissolved organic carbon (DOC) in seawater, the second largest reservoir of carbon in the ocean (Hansell, 2002). Strong correlations between DOC concentration and CDOM absorption have been reported for river-influenced coastal waters at all latitudes (e.g., Massicotte et al., in press and references therein), highlighting the potential usefulness of CDOM to study DOC distributions in these waters.

Despite the important role of CDOM in biogeochemical cycles and as a DOC proxy, our ability to document it *in situ* has been restricted by sea ice in the Arctic Ocean. Since the early 2000s, however, partly due to a significant reduction of summer extent of the Arctic ice pack, a number of *in situ* datasets have been acquired, and recently an Arctic seawater light absorption database was built to provide a synoptic view of the spatial and temporal variations of CDOM in the Arctic Ocean (Matsuoka

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http://dx.doi.org/10.1016/j.rse.2017.08.009
Received 17 December 2016; Received in revised form 25 July 2017; Accepted 4 August 2017

et al., 2014). Still, a large part of the Siberian (or eastern) side of the Arctic Ocean (EAO), where high concentrations of organic carbon are delivered by river discharge (Raymond et al., 2007), was undersampled in the above-mentioned study, which impeded comparing optical properties between the EAO and the North American (or western) side of the Arctic Ocean (WAO). This is an important gap because a very large amount of organic carbon (400 Pg; Pg = 10^{15} g) is stored in the upper three meters of the northern Siberia soils (McGuire et al., 2009) and a significant fraction of this organic carbon may be delivered by river discharge into the Arctic Ocean, which might alter biogeochemical processes of the ocean (e.g., McGuire et al., 2009; IPCC, 2013). We lack knowledge about how the DOC budget of the Arctic Ocean will be modified as a consequence of ongoing global warming. Remote sensing of CDOM provides a powerful mean for tracing DOC in the Arctic Ocean and observing its dynamics and response to climate change from space.

The objectives of this study are therefore 1) to examine optical characteristics of CDOM in the different Arctic seas, 2) establish a relationship between DOC concentration and CDOM absorption coefficient that can be applied to wide range of river-influenced coastal waters, and 3) apply this relationship to satellite-derived CDOM absorption for estimating DOC concentrations from space. With known uncertainties, examples of monitoring of spatial-temporal variability in DOC concentrations for Arctic river-influenced coastal waters are shown at the end of the present study.

2. Materials and methods

The Tara Oceans Polar Circle expedition was conducted from 24 May to 5 November 2013 following a long transect in the Arctic Ocean (Fig. 1a). While the data presented in this study were mainly obtained from the Tara expedition, an Arctic absorption database built by Matsuoka et al. (2014) (hereafter referred to as the M2014 database), is also used here for comparison. Briefly, the M2014 database includes data from Western and Eastern Arctic Ocean covering Beaufort, Chukchi, Kara, and Laptev seas from May to October (Table 1).

To establish a DOC versus $a_{CDOM}(443)$ relationship that is applicable to wide range of river-influenced coastal waters of the Arctic Ocean, we compiled and used publicly available data in addition to the Tara data (Section 2.1.4; Table 1). This provides a confidence of the general relationship in terms of statistics. Similarly, data obtained from MALINA, ICESCAPE2010, ICESCAPE2011 cruises included in the M2014 database (Matsuoka et al., 2014), in addition to Tara data, were also used to evaluate the performance of the CDOM algorithm developed by Matsuoka et al. (2013) (hereafter referred to as gsmA algorithm; see Sections 2.1.5 and 2.2.1).

In the present study, we refer waters having $a_{CDOM}(443) < 0.1\ m^{-1}$ and $> 0.1\ m^{-1}$ as oceanic and coastal waters, respectively. Of coastal waters, these waters are specifically referred to as river-influenced coastal waters when the $a_{CDOM}(443)$ shows a significantly high correlation with salinity or DOC.

2.1. In situ data

2.1.1. CDOM absorption

2.1.1.1. UltraPath measurements. Light absorption coefficients of CDOM using an UltraPath (World Precision Instruments, Inc.) was determined by following the protocols proposed by Bricaud et al. (2010) and Matsuoka et al. (2012). To avoid repeating the protocols, only relevant points to the present study are recalled here. A sample was collected daily from a surface CTD/Niskin bottle or the in-line system flow-through (when no CTD deployment took place) into glass bottles pre-rinsed with MilliQ water. The sample bottles were covered with aluminium foil to avoid a potential effect of light degradation on CDOM in the water. These samples were filtered within a few hours after the sampling using 0.2 μm GHP filters (Acrodisc Inc.) pre-rinsed with 200 ml of Milli-Q water. Absorbance spectra of filtrates were measured from 200 to 727 nm with 1 nm increments relative to a salt solution that was used as a reference. The reference was prepared to have a similar salinity as samples (± 2 salinity units) using Milli-Q water and granular NaCl precombusted in an oven (at 450 °C for 4 h). Abnormally high absorbance values in the near infrared spectral domain were sometimes observed due to the presence of air bubbles in the cell of the sample. These suspicious spectra were removed prior to analysis. While significant effort was made to minimize the difference in temperature and salinity between a sample and reference water during our cruise, this was challenging especially for areas in which waters showed a large salinity gradient with different water temperature. The temperature difference was minimized by placing both the reference and the filtrates at 4 °C in the dark for up to 1 h. The salinity difference was minimized by subtracting the mean value of $OD_{CDOM}(\lambda)$ between 683 and 687 nm ($OD_{null,CDOM}$) from the whole spectrum following Babin et al. (2003) and CDOM absorption coefficients ($a_{CDOM}(\lambda)$, m^{-1}) were calculated as follows:

$$a_{CDOM}(\lambda) = 2.303\frac{[OD_{CDOM}(\lambda) - OD_{null,CDOM}]}{l} \quad (1)$$

where 2.303 is a factor for converting base e to base 10 logarithms, and l is the optical pathlength (m). A 2 m optical pathlength was used for the measurement, except for water having high CDOM content ($> 2.0\ m^{-1}$; Matsuoka, unpublished data) where 0.1 m pathlength was used. Replicates of CDOM absorption spectra were averaged for each measurement.

We acknowledge that scattering due to colloids might have influenced absorption measurement using a long pathlength (> 0.5 m; Floge et al., 2009), which in turn might have influenced CDOM spectra when applying null-correction. However, for Mackenzie river mouth where the highest particle concentrations of the Arctic Ocean are observed (Holmes et al., 2002), Matsuoka et al. (2012) showed that CDOM absorption measurements using an UltraPath with 2-m pathlength were within the instrument resolution from those measured using a Perkin-Elmer Lambda-19 spectrophotometer with 10-cm cell. These results suggest that the impact of colloidal scattering on our absorption measurement can be considered as negligible in the present study.

2.1.1.2. ac-s measurements. To obtain CDOM measurements between those done with the UltraPath, we used a hyper spectral ac-s instrument installed in an automated flow-through system (red crosses in Fig. 1a). Hereafter CDOM absorption coefficients provided by the ac-s are noted as $a^{acs}_{CDOM}(\lambda)$ (in m^{-1}).

Filtered water was pumped through the ac-s (WET Labs) for 10 min per hour (see Boss et al., 2013 for the ac-s setup). The last minute of every 10 min filtered cycle was median-binned and saved. No clean water spectra for calibration were collected with the ac-s during the expedition, and instrument was cleaned weekly. Therefore, the spectra potentially contained errors due to instrument drift (it is acknowledged that the ac family of instrument drifts in time as presented by Twardowski et al., 1999; Temperature and salinity effects are insignificant as we focus here only on the 400–550 nm spectral range; Pegau et al., 1997). To solve this issue, the ac-s data were shifted spectrally to match the corresponding UltraPath measurements in this range. The calibration for ac-s spectra were made by computing and offset between UltraPath and dissolved ac-s measurements done within 25 min:

$$\text{Offset} = a^{UP}_{CDOM}(\lambda) - \text{median}(a^{acs\text{-}obs}_{CDOM}(\lambda)) \quad (2)$$

where $a^{UP}_{CDOM}(\lambda)$ and $a^{acs\text{-}obs}_{CDOM}(\lambda)$ represent CDOM absorption using UltraPath (UP) and ac-s, respectively. There were 59 such matchups within 12 h and 20 km from an UP measurement of dissolved matter, the nearest calibration spectra (in time) was used to correct the spectra:

$$a^{acs}_{CDOM}(\lambda) = a^{acs\text{-}obs}_{CDOM}(\lambda) + \text{Offset(nearest)} \quad (3)$$

The ac-s was then interpolated with 1-nm increments.

A spectral slope (S_{CDOM}, nm^{-1}) was calculated by fitting an